



Corrosion inhibition mechanism of phosphates for early-age reinforced mortar in the presence of chlorides



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ABSTRACT

A study was performed on the corrosion-inhibition mechanism of three phosphate compounds (sodium monofluorophosphate, disodium hydrogen phosphate and trisodium phosphate) for steel rebars embedded in ordinary Portland cement (OPC) mortar exposed to 3% NaCl solutions. The corrosion inhibitors were deployed in two different ways: by migration after the curing period, through the immersion of mortar specimens in aqueous solutions containing the soluble phosphates; and by initial admixture of the phosphate powders in the OPC mortar. The tested specimens were studied using electrochemical corrosion potential and linear polarisation resistance for 70 days of experimentation. A correlation was found between the phosphate content of the specimens (by migration or admixture) and the steel corrosion rate. The results indicate that all the phosphates have the ability to inhibit steel corrosion in mortar.

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1. Introduction

Chloride-induced corrosion of reinforcing steel is one of the most important factors governing the durability of reinforced concrete structures (RCS), particularly in coastal marine environments [1,2]. Many different methods have been employed to mitigate the corrosion risk in RCS, such as barrier layers [3], cathodic protection [4], galvanized or stainless steel rebars [5], and corrosion inhibitors. The latter may be a good way to prevent and/or control reinforcing steel corrosion because inhibitors are easy to apply and less costly than other prevention methods [6–8]. They can be deployed by addition to the mortar or by application on the hardened surface [9].

The use of phosphate compounds as corrosion inhibitors has been widely studied, but there continues to be a lack of consensus about the inhibition mechanism [10,11]. Phosphates offer an environmentally-friendly alternative to traditional and possibly toxic sodium nitrite (NaNO_2) inhibitor [12,13], which has been forbidden in many countries [8]. Soluble phosphates, traditionally sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$) (MFP) or disodium hydrogen phosphate (Na_2HPO_4) (DHP), can be deployed in concrete in two ways: by immersion of the concrete in a phosphate solution or

surface application of a phosphate solution on the hardened concrete by brushing [14,15], or by addition to the cement, sand and water mixture [16]. In the first case the phosphates penetrate the concrete pore network by capillarity, and the efficiency of these methods generally depends on the permeability of the concrete. In all cases, the soluble phosphates react with calcium hydroxide (portlandite) ($\text{Ca}(\text{OH})_2$) to trigger the precipitation of a calcium phosphate, reducing their capacity to act as corrosion inhibitors [17–21], and delaying the setting of cement [2].

In a recent work by the authors [22], a comparative study was performed on the inhibition of steel reinforcement corrosion using MFP, DHP and trisodium phosphate 1-hydrate ($\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$) (TSP) compounds in the absence of chlorides. The three corrosion inhibitors (MFP, DHP and TSP) showed good inhibition behaviour. The order of efficiency for phosphates acting as migrating corrosion inhibitor (MCI) was $\text{MFP} > \text{DHP} > \text{TSP}$, and as admixture corrosion inhibitor (ACI) the best corrosion inhibitor was the DHP compound. Thus it is interesting to investigate the efficiency of these phosphate-based corrosion inhibitors for exposure to chloride containing solutions, as an alternative to traditional nitrite-based compounds.

The aim of this paper is to study the corrosion inhibition mechanism of three soluble phosphates (MFP, DHP and TSP) for reinforced mortar immersed in 3% sodium chloride (NaCl) solutions and to evaluate the effectiveness of the corrosion inhibitors

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application method by migration, through the immersion of mortar specimens in an aqueous phosphate solution, or by initial addition to cement as an admixture.

2. Experimental

Type I 52.5N/SR ordinary Portland cement (OPC) was used with the chemical composition given in Table 1, as determined by X-ray fluorescence. Its particle size distribution (Fig. 1) was determined by laser diffraction, with 10% of the particles being smaller than 1.5 μm , 50% smaller than 10.5 μm , and 90% smaller than 29.2 μm . Carbon steel bars of 8 mm in diameter and a chemical composition (wt.%) of 0.45 C, 0.22 Si, 0.72 Mn, <0.010 P, 0.022 S, 0.13 Cr, 0.13 Ni, 0.18 Cu, and balance Fe were used as reinforcements.

Three soluble phosphates were evaluated: MFP ($\text{Na}_2\text{PO}_3\text{F}$) 95% pure Aldrich, DHP (Na_2HPO_4) 99% pure Panreac, and TSP ($\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$) 97% pure Panreac.

Two types of samples were tested: MCI and ACI specimens. Both had dimensions of 20 mm \times 55 mm \times 80 mm and incorporated embedded steel reinforcement bars.

To assess MCI efficiency, mortar specimens were prepared using a blend of OPC, siliceous sand (SiO_2 , 99% pure) and water with a water/sand/cement ratio of 0.5/3/1. Mortar specimens were used instead of concrete to avoid the formation of large pores by the gravel addition, which could lead to high water content within the pore network and also affect the pathways for chloride and phosphate transport. Two 8 mm diameter carbon steel bars were symmetrically embedded lengthwise in the specimens to act as working electrodes and an external stainless steel cylinder of 50 mm in diameter was placed on top of the specimens to act as counter electrode, with a central drill-hole that allowed the use of a saturated calomel electrode (SCE) as reference. An active surface area of 10 cm^2 was marked on the working electrodes with adhesive tape, thus isolating the triple mortar/steel/atmosphere interface to avoid possible localised corrosion attack due to differential aeration phenomena. The fresh mortar was poured immediately into moulds and cured in conditions of \sim 95% relative humidity (RH) for 28 days at room temperature. After curing, the MCI specimens were fully immersed for 28 days in 0.2 M aqueous solutions of each studied phosphate (MFP, DHP and TSP) or for 28 days in distilled water (blank experiment). It is worth to note that the specimens were fully moist prior to the immersion in the phosphates solution. Finally the specimens were immersed in a 3% NaCl aqueous solution and measurements were performed up to 70 days at room temperature.

The ACI mortar specimens were prepared in the same way as the MCI mortar specimens but adding 3% weight of each phosphate compound (MFP, DHP or TSP) to the OPC powder. A blank specimen without phosphate was also prepared. After curing all the specimens at room temperature for 28 days (\sim 95% RH), they were immersed in a 3% NaCl aqueous solution.

Corrosion behaviour over time was monitored using the electrochemical corrosion potential (E_{corr}) and linear polarisation resistance (LPR) techniques. In LPR tests, the reinforcing steels were polarised to ± 10 mV vs. E_{corr} with a scan rate of 0.166 mV s^{-1} . This allows the steel corrosion current density (i_{corr}) to be calculated using the formula: $i_{\text{corr}} = B/R_p$, where B is a constant and R_p is the value obtained by LPR. To calculate i_{corr} , B values of 26 and

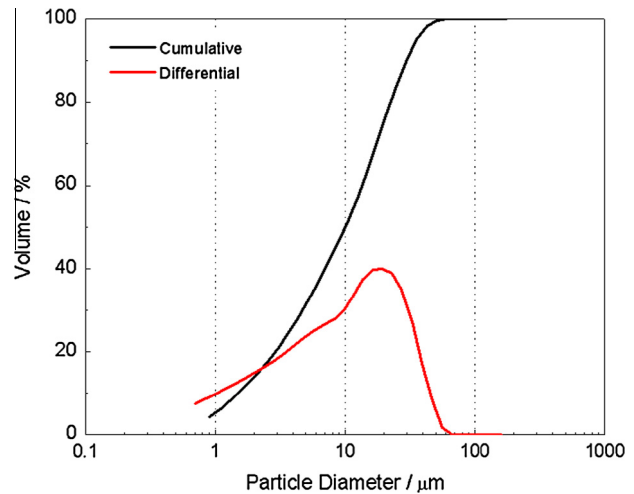


Fig. 1. Granulometry distribution of the tested ordinary Portland cement (OPC) obtained using the laser ray diffraction method.

52 mV were used for specimens with E_{corr} in the active and passive zone, respectively [23]. An EG&G Parc potentiostat model 273A was utilised for electrochemical measurements.

3. Results

Fig. 2 shows the E_{corr} vs. time for steel bars embedded in MCI mortar specimens. The E_{corr} values are situated at levels of low, medium or high risk of corrosion. Even so, the E_{corr} parameter can be used to define the probability of corrosion in these specimens: for $E_{\text{corr}} < -0.27$ V vs. SCE the probability of active corrosion is high (\sim 90%), for -0.27 V $< E_{\text{corr}} < -0.12$ V vs. SCE corrosion is uncertain, and for $E_{\text{corr}} > -0.12$ V vs. SCE there is a 10% probability of corrosion ASTM C 876 [24]. The E_{corr} values for all the MCI mortar specimens in the presence of inhibitor are less negative (noble) than for the blank specimen, except in the case of the specimens immersed in the aqueous TSP solution, which presented a high risk of active corrosion, at least from a qualitative point of view. The specimens immersed in the aqueous MFP solution present the most noble corrosion behaviour, with the least negative E_{corr} value. Accordingly, the E_{corr} values indicate that MFP or DHP may be considered anodic inhibitors that reduce the corrosion rate by increasing the E_{corr} value, for the 0.2 M inhibitor concentration tested.

Fig. 3 shows the i_{corr} vs. time for steel bars embedded in MCI mortar specimens. The i_{corr} values are situated at levels of low or medium risk of corrosion. The dotted line indicates the approximate limit for passive steel values, ≤ 0.1 $\mu\text{A cm}^{-2}$ [25]. The best corrosion inhibitor behaviour is shown by the MFP and DHP compounds, with i_{corr} values of < 0.1 $\mu\text{A cm}^{-2}$, typical of the passive state. The blank specimen was actively corroding.

Fig. 4 displays E_{corr} vs. time for steel bars embedded in ACI mortar specimens. As with the MCI specimens (Fig. 2), the best corrosion inhibitor behaviour is shown by the MFP compound, with E_{corr} values at the medium and high risk of corrosion level. The DHP and TSP compounds show E_{corr} values at the high risk of corrosion level. E_{corr} values for the blank experiment were between -0.3 and -0.5 V vs. SCE, similar to those obtained with the DHP

Table 1
Chemical composition of tested ordinary Portland cement (OPC).

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	TiO_2	K_2O	Na_2O	SO_3	Ignition loss
Mass %	20.33	3.40	4.68	57.84	1.51	0.10	0.09	0.72	0.51	7.26	3.42

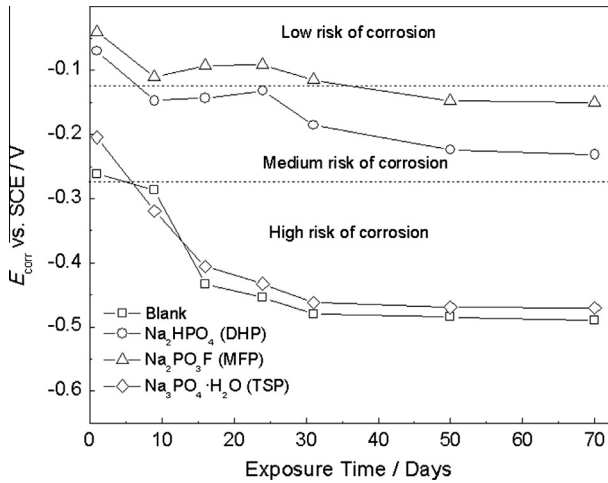


Fig. 2. Corrosion potential (E_{corr}) vs. time for MCI (migrating corrosion inhibitor) specimens. Steel bars embedded in ordinary Portland cement (OPC) mortar and immersed in distilled water (blank experiment) or in 0.2 M aqueous phosphate solution: Na_2HPO_4 (DHP), $\text{Na}_2\text{PO}_3\text{F}$ (MFP) or $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (TSP) and with 3% NaCl.

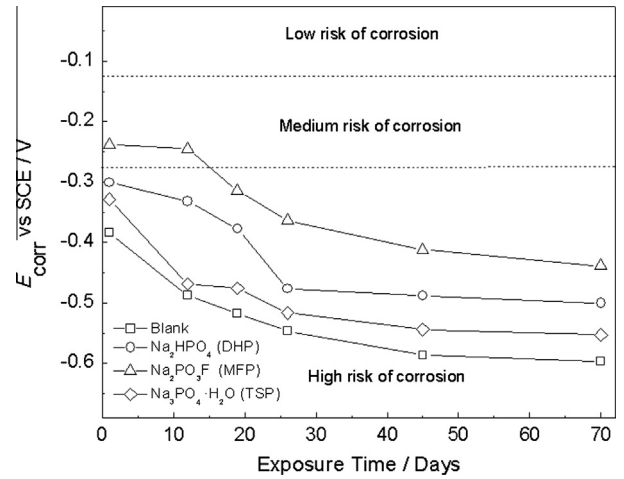


Fig. 4. Corrosion potential (E_{corr}) vs. time for ACI (admixture corrosion inhibitor) specimens. Steel bars embedded in ordinary Portland cement (OPC) mortar mixed with 3% of solid Na_2HPO_4 (DHP), $\text{Na}_2\text{PO}_3\text{F}$ (MFP) or $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (TSP) powder or without phosphates (blank experiment) and immersed in 3% NaCl aqueous solution.

or TSP compound. As with the MCI samples, the specimens prepared by mixing with MFP inhibitor present the most noble corrosion behaviour. Accordingly, E_{corr} values indicate that MFP and to a lesser extent DHP and TSP compounds may be considered anodic inhibitors, for the tested 3% inhibitor weight concentration.

Fig. 5 shows the i_{corr} vs. time for steel bars embedded in ACI mortar specimens. The best corrosion inhibitor behaviour is shown by the MFP compound, with i_{corr} values situated at levels close to a low or medium risk of corrosion. Specimens incorporating the DHP or TSP compounds also showed i_{corr} values situated at a medium risk of corrosion. i_{corr} values for the blank experiment were between 0.3 and $0.9 \mu\text{A cm}^{-2}$, similar to those obtained using the TSP compound.

Fig. 6 shows the inhibitor efficiency (IE) vs. time for steel bars embedded in MCI and ACI mortar specimens. The IE (%) value was obtained using the expression [26]: $IE (\%) = 100 \times (CCD_{abs} - CCD_{pre}) / CCD_{abs}$, where CCD_{abs} and CCD_{pre} are the steel corrosion current densities estimated from R_p measurements in the absence

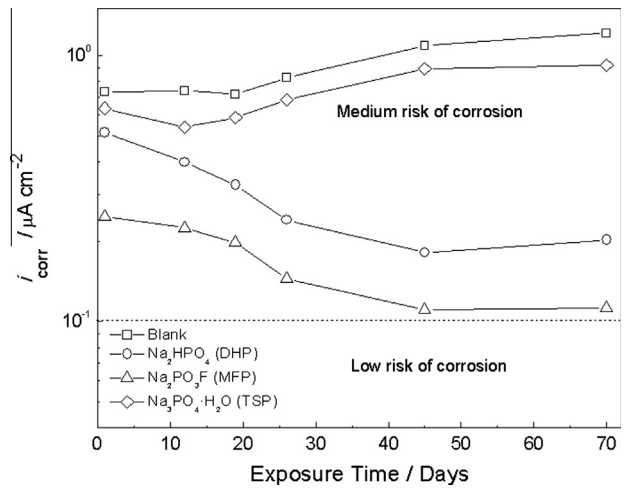


Fig. 5. Corrosion current density (i_{corr}), estimated from R_p measurements, vs. time for ACI (admixture corrosion inhibitor) specimens. Steel bars embedded in ordinary Portland cement (OPC) mortar mixed with 3% of solid Na_2HPO_4 (DHP), $\text{Na}_2\text{PO}_3\text{F}$ (MFP) or $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (TSP) powder or without phosphates (blank experiment) and immersed in 3% NaCl aqueous solution.

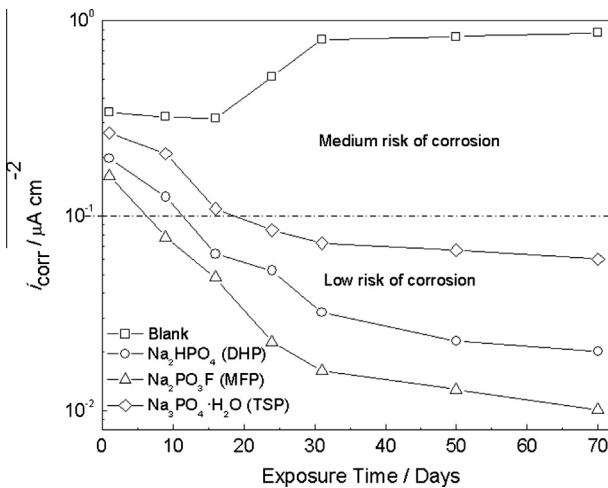


Fig. 3. Corrosion current density (i_{corr}), estimated from R_p measurements, vs. time for MCI (migrating corrosion inhibitor) specimens. Steel bars embedded in ordinary Portland cement (OPC) mortar and immersed in distilled water (blank experiment) or in 0.2 M aqueous phosphate solution: Na_2HPO_4 (DHP), $\text{Na}_2\text{PO}_3\text{F}$ (MFP) or $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (TSP) and with 3% NaCl.

and presence of inhibitor, respectively. In general, for the MCI specimens (Fig. 6 top) the best IE is shown by the MFP compound. Nevertheless, after 50 days of experimentation the MFP and to a lesser extent DHP compounds showed the highest IE , which was $>90\%$ in the case of MFP. In general, the order of IE is $\text{MFP} > \text{DHP} > \text{TSP}$. The ACI specimens showed similar behaviour to the MCI specimens (see Fig. 6 bottom).

4. Discussion

Chloride transport through the mortar pore network and micro-cracks depassivates the oxide film covering the reinforcing steel and accelerates corrosion and mortar deterioration. Advancement of the corrosion process takes place at a rate that depends strongly on the availability of both oxygen and water. The anodic reaction is of particular interest in the case of the presence of chlorides. The anodic process consists of the following steps [5],



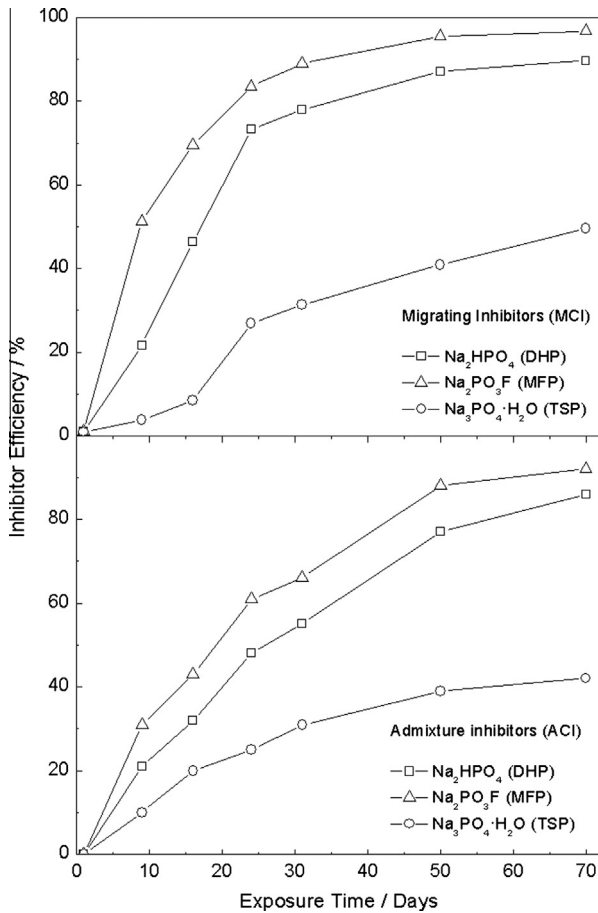
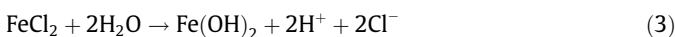
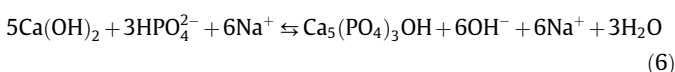
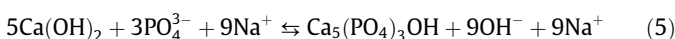
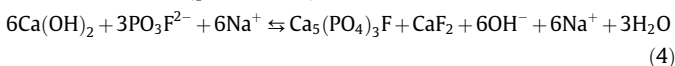


Fig. 6. Inhibitor efficiency (*IE*, %) vs. time for MCI (migrating corrosion inhibitor) and ACI (admixture corrosion inhibitor) specimens. MCI specimens: steel bars embedded in ordinary Portland cement (OPC) mortar and immersed in 0.2 M aqueous phosphate solution (Na_2HPO_4 (DHP), $\text{Na}_2\text{PO}_3\text{F}$ (MFP) or $\text{Na}_3\text{PO}_4\cdot\text{H}_2\text{O}$ (TSP)) for 28 days followed by immersion in 3% NaCl for up to 70 days. ACI specimens: steel bars embedded in OPC mortar prepared adding 3% weight of DHP, MFP or TSP to the OPC powder and immersed in distilled water for 28 days followed by immersion in 3% NaCl for up to 70 days.

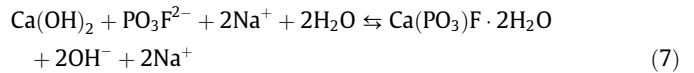


The protective action of phosphate compounds on steel reinforcements may be attributed to the generation of a passive layer of iron phosphate (FePO_4) on the steel rebar due to the precipitation of these compounds. Phosphate ions present in a concrete pore solution may react with iron(III) ions to form strengite ($\text{FePO}_4\cdot 2\text{H}_2\text{O}$) or iron phosphate [8,16,17]. The activity of phosphate ions in the mortar pore solution is determined firstly by the phosphate content and secondly by the presence of portlandite. According to Chaussadent et al. [27], the chemical reactions between the phosphate solution and the substrate (portlandite) are:

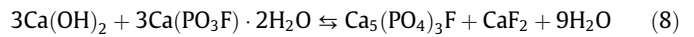


Using the standard free energy values (ΔG_f^0) reported by Wagman et al. [28] and Tacker and Stormer [29] for the different species, it is possible to calculate the equilibrium constants for

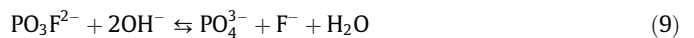
Eqs. (4)–(6), which allow the following activities of phosphate ions in equilibrium with the interstitial solution to be calculated for the MCI specimens: $\log a_{\text{PO}_3\text{F}^{2-}} = -23.02$, $\log a_{\text{PO}_4^{3-}} = -10.81$, and $\log a_{\text{HPO}_4^{2-}} = -11.16$. These activity values are very low to justify the formation of iron phosphate as corrosion inhibitor in the OPC mortar. However, calcium fluorophosphates ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) or calcium hydroxide phosphate ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) may precipitate as amorphous phases which are more soluble than the crystalline phases, and consequently originate a higher activity for phosphate ions [18]. The very low activity value calculated for the PO_3F^{2-} ion in equilibrium, Eq. (4), is not a practical situation. According to the literature [30,31], it is assumed that the reaction between portlandite and sodium monofluorophosphate yields calcium monofluorophosphate dihydrate ($\text{Ca}(\text{PO}_3\text{F})\cdot 2\text{H}_2\text{O}$) and afterwards, according to Ostwald's rule, changes to the more stable fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) according to the following equilibriums [32]:



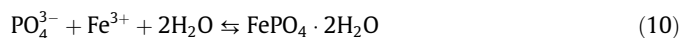
and



Using the ΔG_f^0 for calcium monofluorophosphate dihydrate proposed by Duff [33]: $-2221.29 \text{ kJ mol}^{-1}$, the equilibrium constant of Eq. (7) and the activity of the sodium monofluorophosphate ion were calculated, $\log a_{\text{PO}_3\text{F}^{2-}} = -4.66$. As a result a precipitation mechanism may be proposed. Precipitation of the calcium monofluorophosphate dihydrate phase takes place following an evolution to fluorapatite. Since the PO_3F^{2-} ion is unstable in an alkaline medium [18], it is transformed into a phosphate (PO_4^{3-}) ion according to the equilibrium:



Yielding a high phosphate activity in the medium. Thus, the activity of phosphate ions in the mortar pores is higher than that required for the reaction of iron(III) to generate strengite or iron phosphate:



which act as a protective layer for the steel bar, filling the air voids or microcracks in the mortar. Therefore the use of phosphates gives rise to precipitates with the hydration products of cement, mainly portlandite and C–S–H gel, Eqs. (4)–(8), and the reaction with steel, Eqs. (10) and (11), the latter reaction competing with adsorption of chloride ions on the steel surface. It is noted that further experiments will be required in order to study the optimum phosphate dosage with regard to retardation of the setting process due to the formation of calcium phosphate.

E_{corr} results indicate that the presence of DHP or MFP and to a lesser extent TSP had a positive influence on corrosion inhibition. The E_{corr} was shifted in the anodic direction and the steel/OPC system was less prone to corrosion. E_{corr} values were situated at levels of low or medium risk of corrosion with MCI specimens and a medium or high risk of corrosion with ACI specimens in the presence of phosphate compounds, Figs. 2 and 4, respectively. In contrast, the blank experiment presented a high risk of active corrosion. Comparing the E_{corr} values for MCI and ACI specimens in the presence and absence of inhibitor (Figs. 2 and 4), MFP, DHP or TSP may all be considered anodic inhibitors for the 0.2 M (MCI specimens) or 3% weight (ACI specimens) concentration tested. Contradictory

protection mechanisms have been reported in the literature in relation with phosphate-based inhibitors acting as cathodic inhibitors due to the formation (precipitation) of a film on the steel surface [8], or when the phosphate concentration was lower than the chloride concentration [34]. At a sufficiently high concentration, phosphates may serve as a mixed inhibitor without any change in the E_{corr} value, or an anodic inhibitor in the presence of chloride and oxygen [35,36]. Thus the anodic protection mechanism of the present results may be attributed to the high phosphate concentration (0.2 M or 3%) studied in the presence of chloride ions and oxygen.

i_{corr} values were situated at low or medium levels of corrosion risk, see Fig. 3 for MCI specimens. The dotted line ($\leq 0.1 \mu\text{A cm}^{-2}$) is the approximate limit for the passivity of steel [25]. The best corrosion inhibitor behaviour for MCI specimens was shown by the MFP and DHP compounds. The MCI specimens containing TSP compound were active at the start of the experiment, passivated between 10 and 20 days, and the i_{corr} decreased to the passive state (low risk of corrosion) after 20 days, see Fig. 3. The specimen without inhibitor was active for all the tested time. For the ACI specimens (Fig. 5) the best corrosion inhibitor behaviour was shown by the MFP compound, which presented i_{corr} values close to the passive state.

i_{corr} values (Figs. 3 and 5) indicate active corrosion at the start of the experiment followed by a drop in the corrosion current density which may be associated with the protection afforded by the inhibitor or by the surrounding alkaline medium of the pore network solution. For the MCI specimens, the steel reinforcements were only in the passive state for most of the tested time in the presence of the MFP, DHP or TSP compounds. The DHP compound, which supplied passivity to the steel embedded in MCI specimens (Fig. 3), came in second place. This result is interesting because it suggests that the conventional MFP compound could be replaced by the cheaper DHP.

It can therefore be said that the procedure based on a diffusion process, by immersion in an aqueous phosphate solution, is not the best approach. Preventing corrosion can be well solved by mixing the phosphate compound with the cement paste. This procedure is easy to apply, and a small amount of DHP, of the order of 1%, would probably be enough to protect the steel reinforcement while avoiding any interaction between DHP and portlandite.

The use of corrosion inhibitors is attractive from a prevention point of view because of their low cost, compared to other protection methods such as cathodic protection or the use of galvanized or stainless steel, as indicated above. Corrosion inhibitors can prolong either the initiation period (raising the chloride threshold value or reducing chloride penetration) or the propagation period, according to Tuutti's model [37], reducing the overall corrosion rate.

As a general discussion, the best inhibition efficiency (IE) using migrating corrosion inhibitor (MCI) specimens was shown by the MFP compound. The corrosion inhibition effectiveness in 3% NaCl solutions was lower for ACI than MCI specimens, in particular at early-age for short experimentation times.

5. Conclusions

The residual activity generated by the precipitation of the three studied phosphates (MFP, DHP and TSP) allows the formation of iron phosphate (FePO_4), strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) or amorphous iron phosphate, in combination with iron ions in the medium, so all three phosphates may be appropriate for use as corrosion inhibitors for steel reinforcements in chloride containing solutions (3% NaCl) at early-age. The chemical stability of FePO_4 compounds avoids the formation of FeCl_3 products thus enabling the

application of phosphate-based corrosion inhibitors. Phosphate diffusion is a time-dependent process which decreases with time as the capillary pore network becomes altered by the continuing formation of precipitation products. Furthermore, some phosphate ions will become chemically bound as they penetrate the pore network and form precipitate phosphate compounds.

In general, the best inhibition efficiency (IE) using migrating (MCI) specimens was shown by the MFP compound. The order of IE was MFP > DHP > TSP. These results corroborate the fact that, from a practical point of view, DHP and to a lesser extent TSP compounds are good alternatives (in particular DHP) to the expensive MFP compound for use as migrating corrosion inhibitors. For admixture (ACI) specimens, the best corrosion inhibitor behaviour was shown by the MFP and DHP compounds, which presented i_{corr} values close to the passive state for most of the tested time. The protection mechanism of the three phosphates studied was anodic, increasing the E_{corr} value. The anodic protection mechanism of the present study may be attributed to the high phosphate concentration (0.2 M or 3%) used in relation to the NaCl concentration of 3%. The corrosion inhibition effectiveness was lower for ACI than MCI specimens, in particular at early-age for short experimentation times.

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